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05 December 2016

Version of attached file:

Published Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Le Blond, J.S. and Woskie, S. and Horwell, C.J. and Williamson, B.J. (2017) 'Particulate matter produced during commercial sugarcane harvesting and processing : a respiratory health hazard?', *Atmospheric environment.*, 149 . pp. 34-46.

Further information on publisher's website:

<https://doi.org/10.1016/j.atmosenv.2016.11.012>

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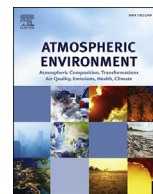
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Particulate matter produced during commercial sugarcane harvesting and processing: A respiratory health hazard?



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HIGHLIGHTS

- Sugarcane burning emissions are known to contribute to poor respiratory health.
- Pre-harvest burning PM could be hazardous to workers and local inhabitants.
- Bagasse ash could be easily broken down to respirable-size PM.
- Cristobalite, a potential toxic mineral, was found in the sugarcane ash samples.

ARTICLE INFO

Article history:

Received 22 July 2016

Received in revised form

1 November 2016

Accepted 5 November 2016

Available online 7 November 2016

Keywords:

Particulate matter

Sugarcane

Respiratory hazard

PM₁₀

Occupational

Ambient

ABSTRACT

Emissions from sugarcane burning are known to impact on the respiratory health of sugar estate workers and local populations. Despite this, there have been few studies on occupational and ambient exposures and risks from airborne particulate matter (PM) associated with field burning and ash re-suspension. From workplace monitoring on sugarcane estates in two different South American countries in 2010 and 2011, median concentrations of airborne PM₁₀ (particulate matter nominally <10 µm in diameter) were found to be statistically much higher during pre-harvest sugarcane burning (1807 µg m⁻³) than during either sugarcane cutting after burning (~123 µg m⁻³) or in the sugarcane processing factory (~175 µg m⁻³). Median PM₁₀ measurements in ambient scenarios, for example in the sugarcane fields before the burning or during 24 h measurements in neighboring villages (bordering the sugarcane plantation), were much lower, between 18 and 37 µg m⁻³. From the analysis of size-selective samples of airborne PM₁₀, collected during sugarcane field burning, cutting and ambient periods, almost all (~96 wt %) fell within the 'respirable' fraction (<4 µm aerodynamic diameter), with a mass median aerodynamic diameter (MMAD) of 1.1 µm. Residual ash from field and bagasse burning, characterised using Scanning Electron Microscopy (SEM) with X-ray elemental analysis, was found to contain carbonaceous and silicate-dominated particles in the PM_{0.5} and PM_{0.5-2.5} size ranges and fibres from <10 to over 50 µm in length. Only a small proportion of the field burning ash (average 0.6 vol %) and bagasse ash (average 1.3 vol %) was in the respirable fraction. However, from grinding experiments, which simulate disaggregation as a result of disturbance during harvest or bagasse ash removal, the ash was fragile and easily broken down into thoracic particulate (<10 µm aerodynamic diameter) and, in some instances, created respirable-sized PM. From exposure calculations, the 8 h time weighted average (TWA) concentrations of PM₁₀, during the different measurement scenarios, were found to be below occupational exposure limits (OELs; 5000 µg m⁻³ for respirable PM). Ambient PM₁₀ exposure of residents surrounding the sugarcane plantations was found to be below the WHO air quality guideline (50 µg m⁻³ as a 24 h mean). The relative risk calculated for 'all cause' mortality from exposure of nearby residents to PM₁₀ generated by sugarcane burning was found to be 3%. The concentrations of PM₁₀ produced during the processing of sugarcane were high (up to 21.5 mg m⁻³), which is concerning given that re-suspended particles of ash in the fields and processing plant have been previously shown to contain potentially toxic cristobalite. PM produced during sugarcane burning, and during extended periods of local exposure to the smoke and re-

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suspended ash, therefore, should be considered as both a potential acute and chronic respiratory health hazard. This issue will become increasingly important with the forecasted rise in sugarcane production for biofuels.

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1. Introduction

In the production of sugar and bioethanol from sugarcane, the burning of leaf (trash) and bagasse increases manual harvesting efficiency and aids in waste disposal. Emissions from agricultural burning practices, however, which include particulate matter (PM), partially combusted carbonaceous matter, carbon biofuels (Rudorff et al., 2010), carbon monoxide (CO), nitrogen oxides (NO_x) and other compounds (Jimenez et al., 2006), are known to impact on the health of local populations (Ribeiro, 2008; Saldiva et al., 1994) and to cause a reduction in air quality (e.g., Dawson and Boopathy, 2007; Cançado et al., 2006). PM, which is the focus of the current study, is generally grouped into different size ranges based on the aerodynamic diameter of particles able to pass, with 50% efficiency, through a specific size-selective inlet head. For PM₁₀ (coarse fraction) 50% of particles of 10 µm are collected, while for PM_{2.5} (fine fraction) 50% of particles of 2.5 µm are collected (US EPA, 1987). Most PM₁₀ can penetrate beyond the extra-thoracic regions (i.e. nasal and mouth cavity), into the bronchial region and so can be considered to represent the particles that would deposit in the thoracic region of the lung (ACGIH/ISO-CEN). The respirable samplers which collect ≥50% of the particles ≤4 µm, represent those particles which if inhaled, can penetrate deeper into the bronchiolar and alveolar unciliated regions of the lung (ACGIH, ISO-CEN, QUARG, 1996).

Although open field burning is known to reduce local air quality, it is thought to be an efficient method for harvesting sugarcane and many plantations therefore opt for it over manual harvesting without burning (and in some cases mechanised harvesting). Sugarcane trash and bagasse burning also takes place in the processing factory, typically as part of the sugar production process and for power generation. Given the recent increase in sugarcane cultivation for the production of ethanol, it is important to understand not only the economic impacts but also the potential health implications of burning sugarcane trash and bagasse in both current and future scenarios.

The aim of this study is to estimate occupational exposure levels to PM₁₀ during the commercial production of sugar from sugarcane and to assess its potential impacts on human health. Sugarcane ash and smoke have also been characterised to determine other factors that could contribute to their toxicity, such as grain size, morphology, mineralogy and elemental composition. The current study adds to the growing literature on the links between mineralogical and chemical properties of particulate from sugarcane burning and potential impacts on human health (e.g., Le Blond et al., 2010).

1.1. Sugarcane burning

Pre-harvest sugarcane burning facilitates and optimises manual crop cutting (Figueiredo and La Scala, 2011) by removing the residue (senescent leaves) and insects (Thorburn et al., 2001). It is carried out in numerous sugarcane-producing countries such as Brazil, Ecuador, China, India and the USA. In São Paulo State, Brazil, for example, during the 2000s, 2 Mha of sugarcane was harvested annually using the pre-burning practice (Rudorff et al., 2010). While

the widespread substitution of ethanol for gasoline was thought to reduce the amount of air pollution (Macedo et al., 2008; IEA, 2004), the recent rise in land used for sugarcane cultivation in Brazil, mainly for biofuel production, caused a significant increase in the number of pre-harvest fires during 2000–2010 (e.g., Arbex et al., 2010). Uriarte et al. (2009) estimated that the sugarcane growing areas in São Paulo State expanded from 2.82 Mha in 2003 to 3.66 Mha in 2007 and resulted in an additional 672 fires compared with 2003. An agreement between the Brazilian Government and large ethanol producers to ban burning by 2013 in the non-mountainous regions, and by 2017 in the mountainous regions (where mechanised harvesting is more challenging) in São Paulo State (Gasparatos et al., 2012), has worked to reduce pre-harvest burning practices. This has had a significant impact in Brazil and, currently, approximately 90% of the sugarcane fields in the South-Central region are harvested 'green' without pre-harvest burning (Nunes et al., 2014). However, pre-harvest burning is still a relatively common practice in smaller-scale plantations, and in other Brazilian states (e.g., Scovronick et al., 2016), as well as in a number of countries in Central America and Africa (Crowe et al., 2009).

An alternative method of trash management is to remove the leaves and burn them in the field after the sugarcane stalks are harvested. This is practised in Louisiana, USA (Dawson and Boopathy, 2007) and Cuba (Frías et al., 2007). Studies in Brazil have shown that approximately 11,000 to 14,000 kg dry mass residues per ha per year are produced and left on the field as a result of 'green' harvesting methods (e.g., Carvalho et al., 2013; Oliveira et al., 1999). In Australia and India, trash blanketing is preferred, where unburned trash is left in the field after harvesting (Robertson and Thornburn, 2007). Trash blanketing can reduce the amount of herbicide needed, encourage soil moisture retention (Kingston et al., 2005) and lessen water run-off and soil erosion (Prove et al., 1995).

In an average processing factory, ~2700 kg of bagasse is generated for each 1000 kg of raw sugar produced from sugarcane stalks (Zandersons et al., 1999). Workers are continuously exposed to dusts from the movement of bagasse as it is transported to the boilers. The heat from the boilers is either used to aid in the sugar evaporation process (co-generation) or to produce steam to drive turbines for electricity generation. A considerable amount of sugarcane bagasse ash (SCBA), formed in the boilers, is routinely dumped in landfills or distributed back onto the sugarcane fields.

1.2. Human exposure and potential health impacts from sugarcane burning

The sugarcane harvesting season typically lasts for six months of the year (e.g., between the dry season, May and October, in Brazil; Cançado et al., 2006), potentially resulting in periods of relatively prolonged and repetitive work-place exposures. In addition, populations residing near areas where sugarcane burning is practised are at risk of exposure to emissions, depending on meteorological conditions. Ambient PM concentrations during the burning season, measured in cities of São Paulo state, Brazil, can be double those of non-burning periods (Arbex et al., 2007), with daily concentrations of PM (and CO) comparable to those in the metropolitan area of São

Paulo city (e.g., CETESB, 1997). In Piracicaba, Brazil (urban), over 60% of ambient PM_{2.5} sampled during the 1997–98 burning season was attributed directly to sugarcane burning (Lara et al., 2005). In a rural locality, near Araraquara (a medium-sized city in the sugarcane-producing region of São Paulo state), clusters of fine PM (0.3–3.0 µm) from sugarcane burning and coarse PM (3.0–10.0 µm) from soil dust resuspension predominated in the winter (pre-harvest burning) season, when compared to the summer (non-burning) season (Caetano-Silva et al., 2013). Spatial techniques to quantify respiratory health effects, have shown that the impacts can be widespread, and the effect on the health of local, non-sugarcane producing populations from nearby sugarcane burning are significant and should not be underestimated (Chargas et al., 2016).

According to Machlis (2002), smoke from sugarcane burning, in relatively low doses, is an annoyance but does not threaten biophysical health. Contrary to this, studies carried out in Brazil have associated pre-harvest burning with an increased occurrence of acute respiratory illness (Arbex et al., 2000), genotoxicity (Silveira et al., 2013) and other diseases of the respiratory system (Lopes and Ribeiro, 2006). Impacts are particularly pronounced in vulnerable groups, such as young children (e.g., Jacobson et al., 2014; Conceição et al., 2001) and the elderly (Cançado et al., 2006), and enhanced in regions where sugarcane cultivation dominates land use (Uriarte et al., 2009). Furthermore, in a study on the island of Maui, Hawaii, there was a clear dose-response relationship, where there was a significantly higher incidence of respiratory distress in smoke-affected areas when greater amounts of acreage were burned (Mnatzaganian et al., 2015). Similarly, a reduction in hospitalisations due to respiratory disease in Brazil is thought to correlate with new state laws that have been instrumental in reducing the practice of pre-harvest burning (e.g., Nicoletta and Belluzzo, 2015).

The findings from animal models are conflicting. In mice, Mazzoli-Rocha et al. (2016) show that exposure to biomass-burning-derived PM (from Araraquara, Brazil) induces lung impairment in a similar way to urban-derived particles (from São Paulo city, Brazil), although it does not cause airway inflammation. In addition, they showed that, for long-term exposures, biomass burning PM may be more toxic than urban-derived particles (Mazzoli-Rocha et al., 2014). However, Silva et al. (2015) argue that other factors, such as temperature and respiratory viruses that occur in the Brazilian winter, may be responsible for the exacerbation of respiratory disease observed during the burning. In addition to health impacts, the smoke plumes can cause substantial reduction in visibility and, as sources of greenhouse gases and ozone, may affect the climate on both a regional and global scale (França et al., 2014).

In regions where sugarcane is harvested manually, cutting is considered heavy physical labour (Lambert et al., 1994; Spurr et al., 1977; Morrison and Blake, 1974). Sugarcane trash ash (SCTA) deposits remaining after pre-harvest burning are trampled on and, therefore, partially broken down so increasing the likelihood of PM ash emissions into the atmosphere. The exposure of workers is relatively high as they are required to cut the sugarcane stalk at its base, close to ground level. The heightened volume of air consumed by manual labourers cutting (burned) sugarcane stalks (~1.95 L min⁻¹, compared with a resting rate of ~0.25 L min⁻¹ in a healthy, 70 kg person; ACSM, 2006) means that the volume of air drawn into the lung carrying SCTA PM is also increased. Nevertheless, the energy expended during manual cutting of burned sugarcane is lower than that during cutting of unburned sugarcane, as the excessive leaf material is removed (Müller and Coetsee, 2008), which is the chief reason sugarcane is still burned on sugarcane estates.

It has been suggested that airborne fly ash from bagasse-fired boilers could also pose a respiratory health hazard (Das et al., 2004; García-Pérez et al., 2002), although the exact nature of the hazard has not been determined and there is very little information on exposure. Another related emission source is SCBA which is often spread on sugarcane fields as a fertilizer or piled in waste dumps and is, therefore, prone to re-suspension by the wind. From experimental production of SCBA, by combusting sugarcane leaf under controlled conditions, residual ash and smoke were found to contain potentially-toxic crystalline silica (Le Blond et al., 2008). This was also detected (using X-ray diffraction, with ~5% detection limits) in SCTA and SCBA samples from several commercial sugarcane estates, however not in PM from pre-harvest burning events (Le Blond et al., 2010). The presence of crystalline silica in SCTA and SCBA highlights the potential for exposure to crystalline silica during activities that re-suspend ash, such as manual harvesting or activities where ash or soil is disturbed.

Of relevance to the current study, although not related to the burning of sugarcane, is the disease bagassosis. This is a form of extrinsic allergic alveolitis caused by intense exposure to fungal and bacterial organisms (such as *Thermoactinomyces sacchari*) living in the dried remnants of bagasse (Phoolchund, 1991). Cases of bagassosis have been reported in sugarcane mills (Hearn, 1968) and may develop in up to 50% of people continuously exposed to mouldy bagasse during the sugarcane-cutting season (Morgan and Seaton, 1984).

As the review, above, demonstrates, few quantitative PM exposure studies have been carried out around sugarcane plantation sites. This study, therefore, offers a unique insight into occupational exposure to PM from sugarcane burning and the ambient exposures experienced by nearby communities.

2. Materials and methods

Two commercial sugarcane-growing estates, one in Ecuador and the other in Brazil, were visited to collect samples of ash and airborne PM during various stages of sugarcane harvesting and processing. Laboratory work was carried out at the Natural History Museum, London, except where stated otherwise.

2.1. Airborne PM concentrations

Airborne PM concentrations were measured with a DustTrak™ aerosol monitor (Model 8520, TSI Inc.) during the following occupational exposure scenarios:

- 1) in sugarcane fields during pre-harvest burns (Burn#, $n = 7$)
- 2) as workers cut the sugarcane (Cutting#, $n = 3$; the next day following burning)
- 3) in the processing factory (Factory#, $n = 2$; where bagasse is burned to provide energy) during hours of operation, at ~1 m from the ground, to provide an estimate of PM exposure for those operating the conveyor belt which transports bagasse to the boilers

In addition, background ambient PM measurements were taken:

- 4) before pre-harvest burning began (Fieldpreburn#, $n = 5$)
- 5) in a nearby village, immediately next to the perimeter of the plantation, during the night (Ambientovernight#, $n = 2$)
- 6) in the same village over ~24 h time periods (Ambient24hr#, $n = 3$).

For the sampling in the village (Ambientovernight# and

Ambient24hr#) the pre-harvest field burning occurred at some point during the evening. Sampling time for the field burning represents the time from fire ignition until extinction of all visible flames in the sugarcane field.

Table 1 details the conditions measured in the fields during the pre-harvest sugarcane burning, including the area burned and ambient temperature. Burns1–5 were in Ecuador whereas Burns6–7 were in Brazil. Meteorological conditions were measured using an Extech RHT10 portable USB data logger (at 30 s intervals averaged over the duration of the fire) at a static point in the field adjacent to that which was being burned. During pre-harvest burning and cutting, workers were closely shadowed and the instruments held at the typical height of a worker's face to mimic occupational exposure.

The DustTrak™ draws in air containing suspended PM at a rate of 1.7 L min⁻¹ through a PM₁₀ inlet head, to measure the concentration of 'thoracic' PM, recording the data every minute (time resolution = 1 min intervals). The measured particle mass concentration (in µg m⁻³) is proportional to the amount of internal light scattering in the DustTrak™, with reference to a calibration factor (Liu et al., 2002) which, in this case, is ISO 12103-1, A1 test dust ('Arizona Road Dust'). The airborne PM measured during this study, however, will have different optical properties to this standard, and hence a corrected calibration factor was used based on outdoor wood smoke (Kingham et al., 2006), which is assumed to represent a suitable analogue for sugarcane particulate. After the correction, a 1 h time weighted average (TWA) was calculated for each of the measurements and then averaged for each of the scenarios (i.e., during the sugarcane burning). TWAs were calculated from the data using the following equation:

$$TWA = \frac{\sum_{i=1}^n C_i t_i}{\sum_{i=1}^n t_i} \quad (1)$$

Where C_i is the concentration during the i th interval and t_i is the duration of the i th interval.

2.2. Airborne PM collection and measurement

Airborne PM was collected with a Sioutas cascade impactor (a portable, size-selective impactor with four individual impaction plates; Sioutas, 2004). Polycarbonate impaction filters (Millipore Isopore™ polycarbonate filters, 25 mm diameter, 0.4 µm pore size) were selected as substrates to enable subsequent analysis of particulate by scanning electron microscopy (SEM; the recommended PTFE filters are unstable under the electron beam). A Leland Legacy pump, operated at 9 L min⁻¹, was used to draw airborne PM into the

impactor and to encourage deposition onto the membranes according to their size. At this flow rate, PM is separated in the following aerodynamic ranges: <0.25, 0.25–0.5, 0.5–1.0, 1.0–2.5 and 2.5–10 µm (based on 50% efficiency, where at least 50% of the material will be less than or equal to the cut-off size). Previously performed particle loading tests showed that, in order for the Sioutas to retain its collection efficiency, PM loading must not exceed 3.14 mg for fine (diameter <2.5 µm) and 700 µg for coarse (diameter between 2.5 and 10 µm) PM (SKC, 2004). Retrospective calculations of the PM loadings on the collection filters showed that these limits were not exceeded during the sampling.

Sampling was carried out concurrently with the DustTrak™ and collections were taken:

- 1) during the pre-harvest burning ($n = 5$)
- 2) as the workers cut the sugarcane ($n = 3$)
- 3) in a nearby village overnight (24 h collection; $n = 2$)
- 4) in the processing factory ($n = 2$).

A Mettler Toledo X5105 dual range balance (with a static discharger) was used to weigh the filters from the cascade impactor before and after PM collection (after conditioning in the same weighing room for a minimum of 24 h to reduce the effects of humidity), to measure the mass concentration of PM deposited on each impactor substrate. The mass median aerodynamic diameter (MMAD; the diameter at which 50% of the particles, by mass, are larger/smaller than the designated cutoff) and the geometric standard deviation (GSD) were calculated for the cascade impactor data according to the measuring scenario from which the samples were collected (i.e., in the field during burning, during cutting etc.).

In the laboratory, a quarter of each of the polycarbonate collection filters from the Sioutas cascade impactor was mounted onto a carbon sticky tab and carbon-coated to a thickness of approximately 25 nm, to ensure electrical conductivity for SEM analysis. The elemental composition and morphology of the airborne PM were investigated in a LEO VP1455 SEM with X-ray elemental analysis (Oxford INCA system), in high vacuum mode and backscattered electron (BSE) mode (WD = 13 mm, EHT = 15 kV). Images were taken on a Philips FEG SEM in secondary electron mode (WD = 8 mm, EHT 10 kV).

2.3. Sugarcane ash and bagasse ash collection and measurement

Bulk samples of SCTA were collected from within burned fields from two commercial sugarcane estates in South America (Burnash#, $n = 7$), which were taken after the sugarcane burn. The bulk sample at each estate consisted of a homogenised mixture of 12

Table 1
Measurement conditions for the airborne particulate monitoring during pre-harvest burning.

Sample number (#)	Area burned (ha)	Date	Local time of fire	Approx. duration of fire (min)	Average ambient air temperature (°C)	Relative humidity (%)	Wind speed (kn)	Wind direction
Burn1	17.1	26/09/08	12:02	43	26	84–87	10	SW
Burn2	12.2	30/09/08	14:09	25	26	82–84	8	SW
Burn3	14.9	01/10/08	14:33	53	26	82–84	11	SW
Burn4	12.3	02/10/08	13:05	61	25	80–83	10	SW
Burn5	10.7	03/10/08	14:09	42	27	82–84	3	S
Burn6	9.5	10/05/07	18:10	47	18	25–27	18	ESE
Burn7	11.4	15/05/07	18:25	62	17	26–27	6	SW

sub-samples collected within each of the seven fields, and were taken from the top 4 cm of ash deposited immediately after pre-harvest burning. The samples were taken from fields that ranged from 9.5 to 17.1 ha, and the burn duration ranged from 25 to 62 min. The two countries had distinctly different meteorological conditions at the time of data collection, with an average ambient air temperature of 26 °C and relative humidity at 83% for Ecuador (Burnash1–5; burning was at midday between 12.00 and 14.00), and an average ambient air temperature of 21 °C and relative humidity at 51% for Brazil (Burnash6–7; burning was after nightfall at ~18.00). Two samples of SCBA were collected from water flushed from the bagasse boilers (Bagasseash#, $n = 2$). For full details of sampling strategy and treatment of these samples see Le Blond et al. (2010).

Particle size distributions of SCTA and SCBA were determined using a Malvern Mastersizer 2000 laser diffractometer (with a Hydro Mu attachment and ultrasonics) at the Department of Geography, University of Cambridge, UK. Prior to analysis, samples were sieved to <1 mm to remove large PM which could damage the particle size analyser. Only the <1 mm fraction was analysed by laser diffraction but the weight data from any sieved particles in the 1–2 mm size range was recorded and re-incorporated into the grain size distribution calculations. Water was used as a dispersant and the following analytical conditions were applied: measurement time 10 s; average 3 cycles; snaps 10000; obscuration range 5–20%; pump speed 2500; ultrasonic displacement 10. The real part of the refractive index (RI) for fly ash samples was varied to provide a sensitivity analysis of the results (Muñoz et al., 2001). The effects of uncertainty in this parameter proved to be small and an RI of 1.73 (real) and 0.1 (imaginary) was selected based on available measurements for fly ash (Cyr and Tagnit-Hamou, 2001). As an additional measurement, the laser diffraction results (that are presented as equivalent spherical diameter) were recalculated to give the aerodynamic diameter, detailed in Equation (2), where d_a is the aerodynamic diameter, d_p is the equivalent spherical diameter, ρ_d is the density of the particles in the sample (in g cm^{-3}) and ρ_o is the unit density (1.0 g cm^{-3}). The density of the particles within the sample was calculated by estimating the composition of the ash/bagasse: 40% silica (2.65 g cm^{-3}), 15% carbon (2.09 g cm^{-3}) and 45% wood dust (5.0 g cm^{-3}).

$$d_a = d_p \sqrt{\frac{\rho_d}{\rho_o}} \quad (2)$$

To test the potential breakdown of the ash due to mechanical disturbance (i.e. 'friability' of the ash), samples of SCTA and SCBA were ground in an agate pestle and mortar for between 10 s and 300 s (5 min). Samples were analysed on the Mastersizer 2000 at each stage of grinding, using the same conditions as above.

2.4. Calculation of the health pertinent fractions

In order to elucidate the proportion of particles that could potentially be inhaled into the respiratory system the data from the cascade impactor (particulate mass) and laser diffractometer (volume %) were recalculated and presented as the proportion of particles within the following size ranges: respirable, thoracic and inhalable. Although PM_{10} is considered approximately equal to the thoracic fraction, the inhalable and respirable fraction were recalculated from the PM data according to the collection efficiency curves (by mass, as defined by International Standards Organization (ISO)/Comité Européen de Normalisation (CEN)/ACGIH respirable convention curve; ACGIH, 2006). As the cascade impactor has a range from 0.03 to $10 \mu\text{m}$ (e.g., Fonseca et al., 2016) only the respirable fraction was calculated.

3. Results

3.1. Airborne PM concentrations

The concentration of PM_{10} was measured with the DustTrak™ during a range of activities and in a number of scenarios during sugarcane processing. Variation in PM_{10} concentration during pre-harvest burning at the 7 different burn sites is shown in Fig. 1. The highest recorded concentration of PM_{10} at any one collection point (1 min averaged intervals) was just over 21.5 mg m^{-3} at site Burn7 (excluding outliers). This pre-harvest burn in Brazil, like that at Burn6, was started at night when ambient temperatures were relatively low ($\sim 17\text{--}18^\circ\text{C}$), whereas the measurements taken in Ecuador (Burn1–Burn5) were conducted during daytime when temperatures were around $25\text{--}27^\circ\text{C}$ (Table 1). In addition, the relative humidity was found to be higher in Ecuador when compared to Brazil, whereas the wind speed was higher (on average) in Brazil. The average values for the PM_{10} concentrations pre-harvest burning in Ecuador were lower ($1835 \mu\text{g m}^{-3}$), compared with those measured in Brazil ($2791 \mu\text{g m}^{-3}$). In addition, the 1 h TWA for PM_{10} concentrations collected in Ecuador were less than Brazil (with average median values of 386 and $568 \mu\text{g m}^{-3}$, respectively). However, the number of measurements is limited and Burn7, the pre-harvest burning scenario found to produce the greatest PM_{10} concentration, was collected at a site where the temperature, relative humidity and wind speed were comparatively low (17°C , 26–27% and 6 knots, respectively).

When the different measurement scenarios (i.e. measurement in the field during burning, during ambient periods etc.) were compared, pre-harvest field burning produces the highest concentration of 1 h TWA for PM_{10} with a geometric mean = $1807 \mu\text{g m}^{-3}$ (Fig. 2). The statistical significance was determined among the measurement scenarios by one-way ANOVA ($F(5,16) = 21.8$, $p < 0.001$). A Tukey post-hoc test ($\alpha = 0.05$) revealed that the PM_{10} 1 h TWA measured during the field burning was significantly higher than all other measurement scenarios and ambient conditions measured. There was no statistically significant difference between the TWA calculated for the other measurement scenarios.

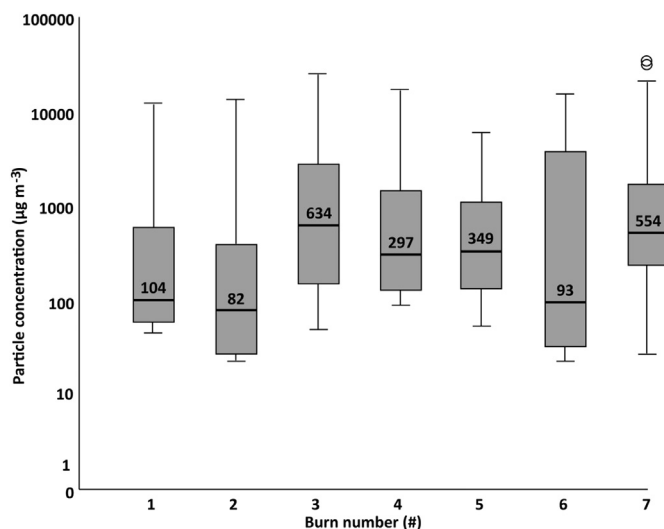


Fig. 1. PM_{10} concentrations from the DustTrak™ aerosol monitor during pre-harvest sugarcane field burns at 7 sites (Burn number). Median values are labelled inside the 25th to 75th box plots, and outliers are identified by circles.

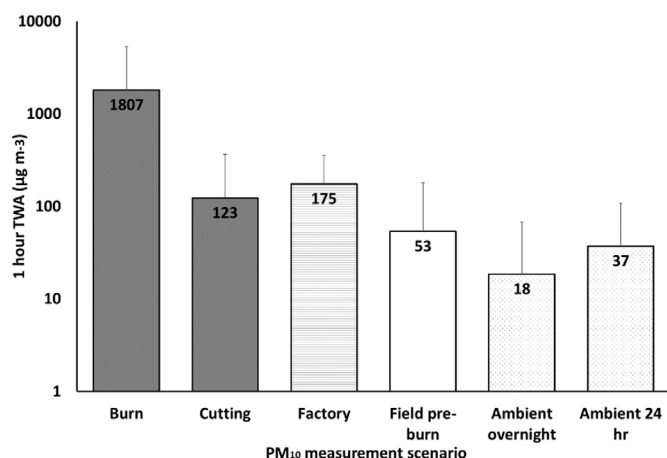


Fig. 2. Comparison of the 1 h TWA calculated for the different activities and ambient environments during sugarcane cultivation (using the geometric mean for each measurement scenario), with the maximum 1 h TWA shown by positive line above.

3.2. Airborne PM (mass) collection

The average total concentration of PM₁₀ collected on the filters in the Sioutas impactor (after normalisation for the volume of air sampled) was greatest during processing factory operations (4006 µg m⁻³). This was closely followed by concentrations during sugarcane pre-harvest burning (3833 µg m⁻³), then sugarcane cutting (2251 µg m⁻³) and then in the overnight ambient environments (1449 µg m⁻³). The majority of the PM₁₀ mass collected during the sugarcane burning (Fig. 3a), cutting (Fig. 3b) and overnight sampling (Fig. 3d) was <0.25 µm aerodynamic diameter, whereas in the processing factory (Fig. 3c) it was predominantly 0.25–0.50 µm. The proportion of respirable PM also varied among collection scenarios, with field burning, sugarcane cutting and ambient overnight collections containing ~96% PM₄ compared with 76% from the processing factory (Table 2). The mass median aerodynamic diameter (MMAD) of the thoracic fraction is relatively low

for the field burning, sugarcane cutting and ambient overnight (all 1.1 µm), but higher for the material collected in the processing factory (1.5 µm).

A synoptic view of the particles collected on the filters during the pre-harvest burning, by SEM, shows an array of mineral components clustered together, many of which could be considered thoracic in size (PM₁₀). An elemental map (Fig. 4) shows the clustering of angular mineral phases collected during pre-harvest burning, with numerous particles composed of silicate phases with minor sodium, potassium and aluminium.

Point SEM-EDS analysis showed that most particles on the filters were predominantly composed of carbon (Fig. 5). Analysis of PM in pre-harvest burning filter collections identified carbonaceous material, silica-dominated particles, silicate phases and other compounds, such as KCl (Fig. 5a) and NaCl (Fig. 5b). Metal oxides, including Mg and Fe oxides, were also present. PM was generally irregularly shaped and contained minerals commonly found in soils (*i.e.* silicates; Fig. 5c). Some remnants of raw plant material were also observed on some of the filters from pre-harvest burning and cutting collections, including phytoliths (Fig. 5c) and fibrous relics. The fibres have a ratio of length to width greater than 3:1 (and in some cases 5:1) and range in size from <10 to over 50 µm in length.

Carbonaceous material on the PM filters collected during pre-harvest burning and subsequent cutting were visibly charred, whereas the majority of carbon on filters collecting in the factory was unburned and resembled the original bagasse material. The exceptions were sub-micron carbon particles (Fig. 5d), which can be described as fractal-like aggregates similar to those typically produced from wood combustion (*e.g.*, Gwaze et al., 2006).

3.3. Ash grain size distributions

All of the seven SCTA samples, taken from Brazil and Ecuador, contained particles with similar size ranges, with means of 0.6% respirable, 1.7% thoracic and 16.0% inhalable material (in cumulative vol. %; Table 3). The SCBA samples were dissimilar, with Bagasseash1 containing a greater proportion of particles in all the health-pertinent size ranges and containing the greatest proportion of respirable material in the suite of samples (2.6%).

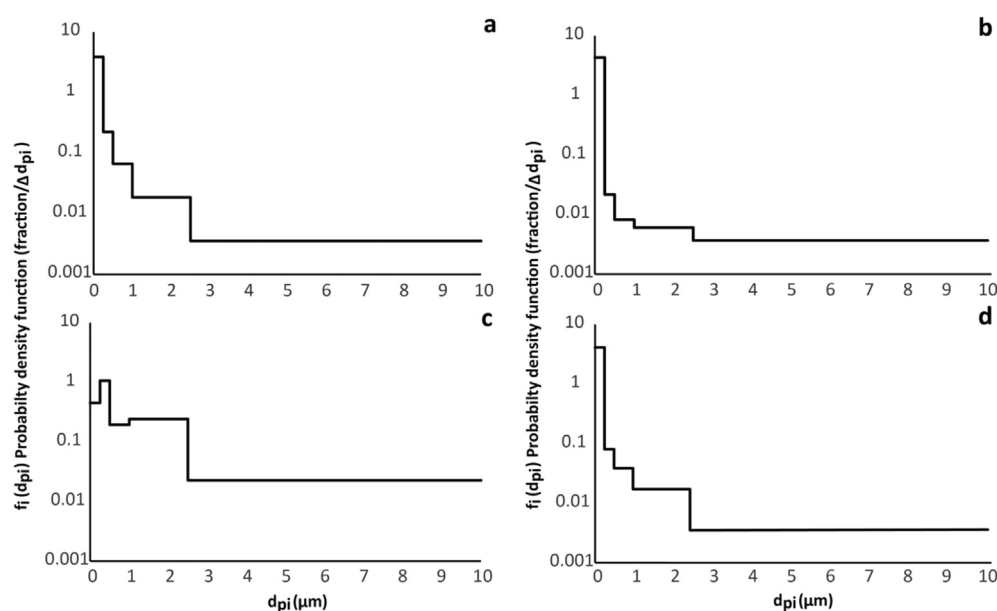


Fig. 3. Mass of collected by the Sioutas impactor stages during: a) pre-harvest burning; b) sugarcane cutting; c) processing factory; d) ambient overnight collections. NB. The scenarios 'before cutting' and 'ambient full day' were not sampled by the Sioutas cascade impactor.

Table 2
Proportion of respirable PM and MMAD (within the PM₁₀ fraction) for each measurement scenario.

	Respirable (wt%)	Mass median aerodynamic diameter (MMAD) within for the PM ₁₀ fraction (μm)
Pre-harvest burning	96.0	1.1
Sugarcane cutting	96.1	1.1
Processing factory	75.8	1.5
Ambient overnight	96.4	1.1

Conversely, Bagasseash2 contained the least amount of particles (by volume) within each size fraction, and had just 7.4% in the inhalable fraction.

Grain size distributions shift to a smaller distribution for both SCTA ($n = 2$) and SCBA ($n = 2$) samples after grinding (Fig. 6). In both SCTA samples the shape of the particle distribution becomes bimodal after grinding, with a clear increase in the proportion of particles in the smaller size ranges. For the SCBA Bagasseash1 is more prone to particle reduction after grinding when compared with Bagasseash2.

The proportion of all health-pertinent size fractions increases

after grinding, with the largest increase in the respirable fraction occurring after 300 s grinding SCBA Bagasseash1 (48.9% increase; Table 4). The sample that was least affected by grinding was the SCBA Bagasseash2, which showed a 1.7% increase in respirable material in the ash sampled after 300 s of grinding.

3.4. Approximated PM exposure and dose

The ‘ventilator rates’ for adults were used to attempt to calculate acute PM exposure levels over a working day. An estimation has been made for the ventilation rates, based on the intense physical

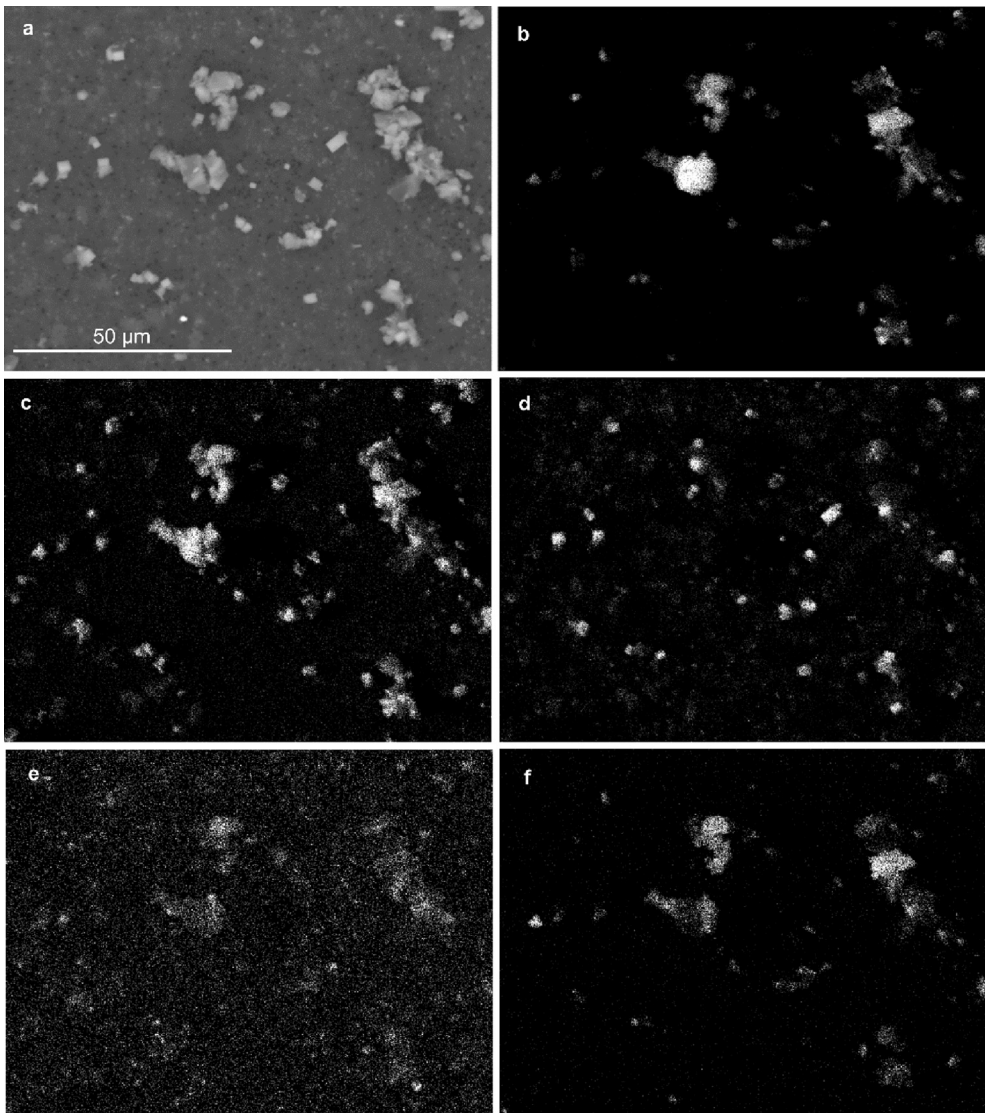


Fig. 4. a) SEM-EDS image of particles collected on polycarbonate filters (from Sioutas collections) from the pre-harvest burn Burn1. b–f) Qualitative X-ray elemental maps (SEM-EDS) for the same area as in Fig. 4a showing the presence and distribution of b) Si, c) O, d) Na, e) K and f) Al. Image grey scale is from black (not detected) through to relatively high concentrations (white).

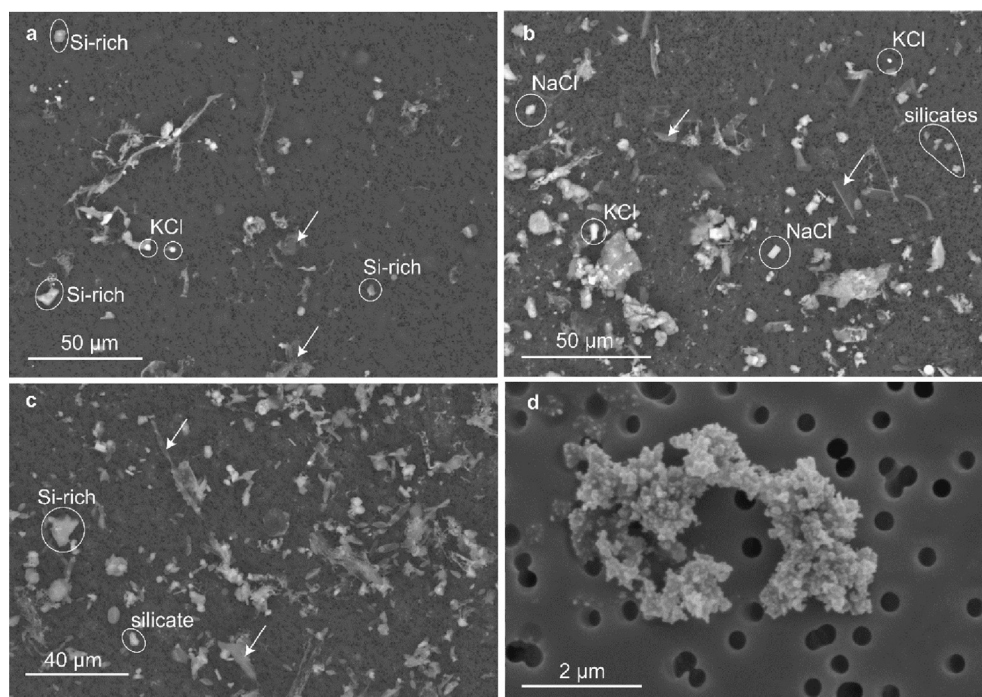


Fig. 5. SEM BSE images of PM collected on polycarbonate filters (from Sioutas collections) from field sampling of pre-harvest burning a–c: a) Burn7 and b) Burn5, c) during sugarcane cutting ‘Cutting1’; and d) in the processing factory ‘Fabrica1’. The arrows indicate carbonaceous material, as identified by SEM EDS point analysis.

Table 3

Size fraction of PM in ash samples measured by laser diffraction (in cumulative vol. %), defined by health-pertinent size fraction (using the aerodynamic diameter).

Size fraction	Burnash1	Burnash2	Burnash3	Burnash4	Burnash5	Burnash6	Burnash7	Bagasseash1	Bagasseash2
Respirable	0.6	0.6	0.6	0.5	0.6	0.7	0.7	2.6	0.1
Thoracic	1.7	1.6	1.5	1.5	1.7	1.8	1.8	6.8	0.6
Inhalable	16.7	14.5	15.0	15.1	16.9	18.5	14.9	29.0	7.4

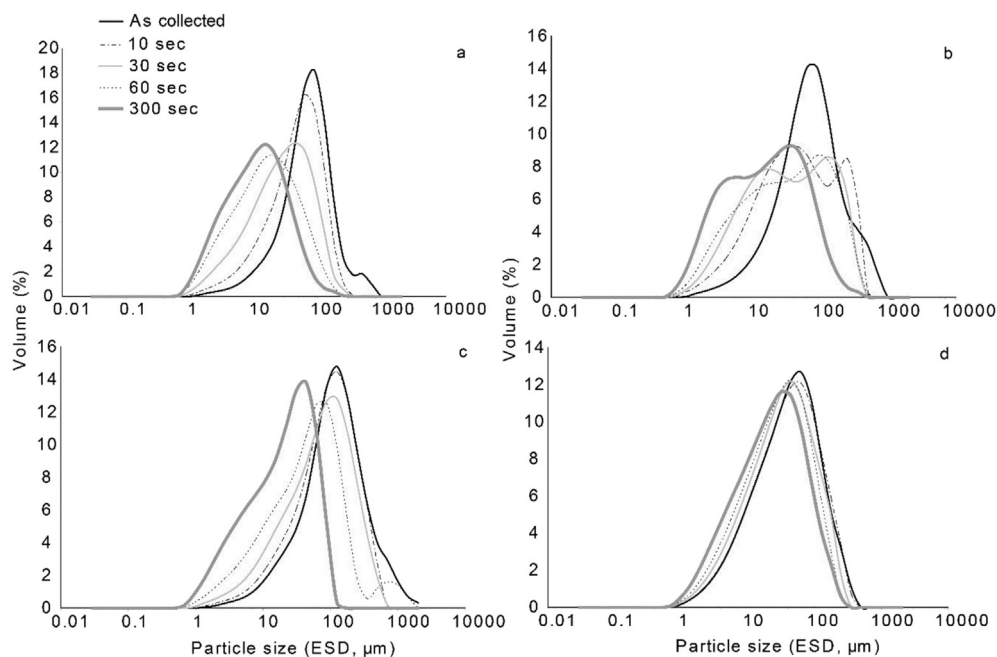


Fig. 6. PM grain size of ash ‘as collected’ (with potential breakdown after transportation) and after grinding for different periods of time, for SCTA a) Burnash1 and b) Burnash7 and SCBA c) Bagasseash1 and d) Bagasseash2. ESD = equivalent spherical diameter.

Table 4

Size fractions of re-ground SCTA and SCBA samples (after grinding for 300 s; using the aerodynamic diameter).

Size fraction	Burnash1		Burnash7		Bagasseash1		Bagasseash2	
	After grinding (vol %)	% increase from 'as received'	After grinding (vol %)	% increase from 'as received'	After grinding (vol %)	% increase from 'as received'	After grinding (vol %)	% increase from 'as received'
Respirable	10.7	6.0	11.3	5.8	5.2	48.9	7.1	1.7
Thoracic	22.7	7.7	21.0	8.7	12.5	54.0	14.7	4.0
Inhalable	42.6	39.2	36.2	41.3	35.5	81.7	35.5	19.5

activity required for manual cutting and harvesting (e.g., Barbosa et al., 2012). In these calculations, a highly active adult male (defined as ~23–30 years old) has a daily ventilation rate of ~22 m³ day⁻¹ (e.g., Brown et al., 2013; Brochu et al., 2006). During an 8-hour shift, burning sugarcane in the field, an active adult male would have an 8 h TWA exposure of 2147 µg m⁻³ PM₁₀ and is predicted to have a dose of ~16000 µg of PM₁₀ during the shift. Considering that PM₁₀ can be equated with the thoracic fraction (e.g., ACGIH, 2006), we can estimate that the majority of this calculated PM burden will be thoracic. Further to this, from the results of the PM collection onto the cascade impactor, ~76–96% of thoracic fraction is respirable, which would equal a dose of ~15000 µg of respirable PM every 8 h shift. However, an 8 h shift spent burning is unlikely, and burning/harvesting practices tend to vary widely among different countries and plantations. One possible scenario would be a shift working 7 h cutting and 1 h sugarcane burning, where an active adult male would be exposed to an 8 h TWA concentration of 402 µg m⁻³ PM₁₀. This is based on a dose of ~3000 µg of PM₁₀ during the shift, of which ~2800 µg would be respirable. For an 8 h shift in the processing factory, an active adult would be exposed to an 8 h TWA concentration of 152 µg m⁻³ PM₁₀ and have a dose of ~1300 µg of PM₁₀ (~1000 µg respirable PM). The total 24 h PM₁₀ TWA concentration averaged for an 8 h shift of solely sugarcane burning, and 16 h of exposure to ambient PM is 746 µg m⁻³. Similarly, the 24 h PM₁₀ concentration averages for an 8 h shift, including sugarcane burning (1 h) and cutting (7 h) and 16 h of exposure to ambient PM, is 164 µg m⁻³. In the processing factory over the same time period and with 16 h of exposure to ambient PM, the concentration average would be 89 µg m⁻³.

To estimate the mass dose of ambient PM₁₀ inhaled by residents near to the sugarcane plantation (not employed in the sugarcane industry) over a 24-hour period in a rural setting, median (average activity) daily 'ventilator rates' for adult males (~17 m³ day⁻¹), females (~14 m³ day⁻¹) and children aged 7–11 years (average of male and female children; ~10 m³ day⁻¹) were used (ventilator rates from Brown et al., 2013; Brochu et al., 2006). PM₁₀ dose was 806 µg day⁻¹ for adult males, 630 µg day⁻¹ for adult females and 471 µg day⁻¹ for children. The 24 h TWA exposure for people exposed to ambient levels of PM₁₀ from near to the sugarcane fields (calculated from the full day PM₁₀ collections) was 46 µg m⁻³.

Using the data from the ambient 24 h PM₁₀ collection, we can calculate an approximate relative risk for estimating the attributable burden at any measured concentration using the following equation (Osto, 2004):

$$RR = \exp[\beta(X - X_0)] \quad (3)$$

Where β is 0.0008 and represents the mortality effects (assuming an increase in short term, 24 h, exposure of 10 µg m⁻³ PM₁₀ causes an increased risk of between 0.6 and 1.0%; Osto, 2004). When calculating the ambient exposure to people residing near the sugarcane fields, X is the measured concentration of 46 µg m⁻³ and X_0 is the baseline PM₁₀ concentration (the level that would exist without any man-made pollution, estimated to be 10 µg m⁻³ PM₁₀; Osto, 2004). The RR is calculated as 1.03 (95% CI 1.02, 1.04), hence

after short term exposure to PM₁₀ from sugarcane burning the risk of 'all cause' mortality is increased by 3%.

4. Discussion

4.1. Occupational PM exposure and dose

This study has shown that a substantial amount of PM₁₀ is released during sugarcane burning. The amount of PM₁₀ produced is statistically higher than the other PM-generating scenarios measured in this study, which suggests that the labourers employed in initiating the fires, and maintaining a steady burn rate, will potentially be exposed to the greatest burden of PM₁₀. An 8 h shift solely in the sugarcane burning fields is possible, but unlikely, as typically one field is burned at any one time (although harvesting techniques vary between countries and plantations). In the case of an 8 h shift pre-harvest burning, the average calculated 8 h TWA for PM₁₀ is 2147 µg m⁻³, which is less than the 8 h permissible exposure limit (PEL) issued by OSHA (5000 µg m⁻³ for respirable PM, and 15000 µg m⁻³ for total PM; OSHA, 2006). However, authors citing research on dusts that are considered inert believe that these occupational exposure limits (OELs) are too high and may not fully protect against pulmonary damage (e.g., Cherrie et al., 2013).

The estimated dose of PM₁₀ varied for each of the measured scenarios. For example, the mass of the thoracic fraction of PM that an adult male would be exposed to during an 8-hour shift working on sugarcane burning was found to be 15825 µg, whereas a similar 8 h shift in the processing factory would result in a dose of 1290 µg over the entirety of the shift. There are no comparable metrics by which to compare the dose of PM (i.e., mass) that may enter into the thorax and beyond into the deeper region of the lung, the closest comparator being coalminers. Interestingly, coalminers exposed to significant levels of dust do not experience 'lung overload' (described as a saturation of the capability of alveolar macrophages to ingest particles; Kuempel et al., 2001; Tran and Buchanan, 2000) or elevated lung cancer risks (e.g., Stayner and Graber, 2011; Morfeld, 2013). However, a correlation can be found between exposure to coal mine dust and coal worker's pneumoconiosis (Morfeld et al., 2015). Coal worker's pneumoconiosis is not a response to a specific mineral within the coal dust (although silicosis can develop if the coal dust is rich in crystalline silica; Derbyshire et al., 2012) but, rather, by chronic exposure to high concentrations of insoluble respirable particles.

Sampling locations with higher ambient temperatures (e.g., Ecuador, 25–27 °C) show elevated levels of PM₁₀ (averaged) during field burns than those with lower temperatures (e.g., Brazil, 17–18 °C). However, the burn producing the highest concentration of PM₁₀ was in Brazil, where the lowest temperature, relative humidity and wind speed were recorded. Further to this, the other measurements made ($n = 2$) in Brazil were during a period of high wind speed (18 knots), which may have contributed to the reduced PM₁₀ concentration measured. Due to the limited number of measurements, no firm associations can be drawn between the PM and the meteorological conditions observed during this sampling.

4.2. Ambient PM exposure

Ambient PM₁₀ guidelines are typically quoted as a PM₁₀ concentration (in $\mu\text{g m}^{-3}$) over a 24 h or annual averaging period. The World Health Organization (WHO) has an ambient air quality guideline of $50 \mu\text{g m}^{-3}$ for PM₁₀, averaged over 24 h (WHO, 2005). In the US, the Environmental Protection Agency (EPA) issues National Ambient Air Quality Standards (NAAQS) limits for PM₁₀ in the environment of $150 \mu\text{g m}^{-3}$ averaged over 24-hours, which must not be exceeded more than once a year, on average, over a period of three years (US EPA, 2013). As pre-harvest burning and cutting occurs in an outdoor environment, air quality in exposed communities residing near the sugarcane fields should not exceed these guidance levels for ambient PM₁₀.

Data collected in this study during ambient periods (either between burning or for periods of time in locations outside of the sugarcane plantation site) reveal that PM₁₀ levels measured during sugarcane burning (averaging $\sim 45 \mu\text{g m}^{-3}$) did not exceed WHO guidelines. However, another study noted that the PM₁₀ concentrations measured in Araraquara, Brazil exceeded the WHO guidelines on 103, 84 and 33 days in 2010, 2011 and 2012, respectively (Souza and Nascimento, 2016), although there will be substantial differences between the PM₁₀ levels measured in rural (as measured in this study) and urban environments. PM₁₀ concentrations measured in São Paulo city during August 7th–28th 2008 (during the dry, sugarcane burning season), for example, had an average of $64 \mu\text{g m}^{-3}$ over a 24-hour period (Souza et al., 2014), which is thought to be influenced by sugarcane burning in the areas surrounding the city (Vasconcellos et al., 2010). Previous studies have shown a link between adverse health effects in city populations with episodes of sugarcane burning (e.g., Umbuzeiro et al., 2008; Carvalho-Oliveira et al., 2005).

Populations with pre-existing respiratory disease are particularly at risk after exposure to inhalable particles from sugarcane and other forms of agricultural burning. Agricultural burning (straw and stubble) was found to increase the PM₁₀ concentrations (determined from the 24 h integrated concentration of PM₁₀) measured on the outskirts of Winnipeg, Canada, from 15 to $40 \mu\text{g m}^{-3}$ in the non-burning season (June to September) to 80 – $110 \mu\text{g m}^{-3}$ in the burning season (September to October). People with pre-existing respiratory disorders, such as chronic bronchitis and asthma, were notably more susceptible to the smoke (Long et al., 1998).

4.3. Airborne PM characteristics

When considering the PM₁₀ particles collected using the Sioutas cascade impactor, the total masses varied from location to location, as follows: processing factory > pre-harvest burning > sugarcane cutting > ambient overnight collections. The MMAD for the PM₁₀ collected on the cascade impactor filters was $1.04 \mu\text{m}$ during the sugarcane field burning and $2.13 \mu\text{m}$ in the processing factory. Previous studies have found that the majority of particles, in terms of particle number, emitted during biomass burning events are ultrafine (i.e., $<0.1 \mu\text{m}$; Morawska et al., 1998). In terms of mass, much of the PM released by biomass burning is thought to be $<2.5 \mu\text{m}$ in aerodynamic diameter (US EPA, 1998). Smouldering combustion tends to release large amounts of fine PM, whereas, the burning efficiency is greater during flaming combustion and hence the amount of PM released is comparatively less (Ward, 1990). The higher concentrations of PM_{0.5} and PM_{0.5–2.5} (i.e. ultrafine and fine PM) released during pre-harvest burning may, therefore, have been produced by smouldering plant material in the field (see Le Blond et al., 2010, Fig. 4), whereas flaming conditions (i.e. regulated temperatures) in the boilers at the processing plant (producing the bagasse ash) would be more likely to generate larger-sized PM.

Although there is no combustion occurring during sugarcane cutting, the presence of abundant fine PM (over 96% of the PM collected on the cascade impactor filters was respirable) suggests that the ash remaining on the ground after burning is easily broken down into smaller fragments and lofted into the air. While the concentrations of PM₁₀ collected during the sugarcane cutting and ambient overnight collections were less than the mass of PM₁₀ collected during field burning, the proportion of respirable PM is similarly high ($\sim 96\%$). Ground ash therefore represents a source of PM₁₀ that could be lofted into the air and become a chronic problem for communities residing near sugarcane fields.

4.4. Ash characteristics

During biomass burning, ultra-fine mode or fine mode particulate is formed from either condensation of pyrolysis products, complex aggregation processes that form black carbon (soot) particles or oxidation of emitted volatile organic gases (Cashier, 1998). Carbonaceous material was abundant in PM collected during both pre-harvest burning and harvesting, and is a common component emitted from biomass burning (e.g., Andreae and Merlet, 2001), including PM from other silica-rich biomass burning, such as rice straw burned in the field (Hayes et al., 2005). Carbonisation is typically characterised by the disappearance of chemical bonds and the creation of low-molecular weight compounds, resulting in char containing carbon, hydrogen and mineral oxides (Bilba and Ouensanga, 1996).

During vaporisation, airborne particles undergo surface enrichment, via condensation or reaction, in heavy metals and other compounds (such as KCl). Nucleation of compounds can occur, for example Zn oxide, K₂SO₄, KCl and K₂CO₃ (Oberberger and Brunner, 2005). In this study we observed particles composed of salts by SEM (KCl and NaCl). Sylvite (KCl) was frequently observed in PM from pre-harvest burning and harvesting, and has also been previously identified in both coarse (i.e. PM_{2.5–10}) and fine aerosol collected during sugarcane burning in Brazil (Allen et al., 2004) and in smoke samples collected from burning savannah grasslands (predominantly) in southern Africa (Liu et al., 2000). PM emissions from open-air wheat residue burning were also noted to be enriched in KCl (Hayes et al., 2005), a soluble salt that has been shown to exhibit a relatively high bio-accessibility from metal smelter emission sites (e.g., Mbendge et al., 2015) but low toxicity. The aggregated sub-micron spheres present on the filters collected in the factory are most likely primary soot particles, which are characteristic of flaming conditions rather than smouldering combustion (Cashier, 1998) and hence may originate from the boilers in the processing factory. These particle aggregates are known to be composed of graphite layers, occasionally with inclusions of minerals such as silica or K-salts (e.g., Li et al., 2003; Pósfai et al., 2003; Wentzel et al., 2003).

From SEM analyses, fibrous material was present in the airborne PM collected from most of the sugarcane processing activities. The aspect ratio of these fibre-like particles conforms to the WHO definition for fibres used by regulatory authorities in their classification and measurement of asbestos (WHO, 1986). However, we suggest that these fibre-like particles cannot be described as asbestiform – a term employed to describe minerals in which fibres have a high tensile strength and flexibility, and are insoluble in the lung.

The majority ($\sim 84\%$) of the bulk SCTA is too large to be inhaled ($>10 \mu\text{m}$) and would not present an immediate hazard to human health. Only $\sim 2\%$ of the total volume of one of the SCBA samples (Bagasseash1) was small enough (i.e. $<4 \mu\text{m}$) to be inhaled deep into the alveolar regions of the lung. The bimodal grain size distribution in the ash, observed most prominently in sample

Burnash7, may be indicative of the two types of material present in the sugarcane trash ash: unburned plant material and carbonaceous char. Char will tend to breakdown much more readily than unburned plant material, yielding a peak in the grain size distribution at smaller particle size.

Re-grinding experiments showed that the sugarcane ash is friable and can be broken into finer PM by mechanical disturbance (with an average increase of ~6% in the respirable fraction after 5 min of grinding), which could be inhaled by manual labourers when they harvest the sugarcane stalks. In the case of Bagasseash1 (SCBA) there was a 49% increase in the proportion of respirable PM produced after 5 min of grinding. This is particularly important, as the quantities of SCBA produced during the sugar-production process can be significant (e.g., ~2700 kg bagasse for every 1000 kg of raw sugar produced; Zandersons et al., 1999). SCBA is regularly left in storage heaps and is, therefore, vulnerable to erosion or re-suspension by the wind or during transportation. Other activities that may break down the ash include re-distribution over sugarcane fields as a fertilizer, or use as an additive in the manufacture of other materials such as concrete.

4.5. Relative risk calculations

The RR calculations for short term exposure to ambient levels of PM₁₀ in the sugarcane burning areas measured here, indicate that there could be a 3% increase in 'all cause' mortality due to an increase in the estimated risk of 0.8% per additional 10 µg m⁻³ PM₁₀ (from Osto, 2004). In comparison, findings reported by the Committee of the Environmental and Occupational Health Assembly of the American Thoracic Society (1996) suggest that for each 10 µg m⁻³ increase in PM₁₀ total mortality increases by 1%, respiratory mortality by 3.4% and cardiovascular mortality by 1.4%. Other studies have estimated higher relative risk values for more specific health outcomes. For example, Souza and Nascimento (2016) found that an increase of 10 µg m⁻³ PM₁₀ in Araraquara, Brazil, resulted in a 15% increase in relative risk of hospitalization due to pneumonia. Similarly, in studies monitoring the impacts from residential wood burning in Seattle, USA, a 3.7% increase in emergency room visits for asthma was observed for every 10 µg m⁻³ rise in PM₁₀ (Schwartz et al., 1993).

5. Conclusions

PM exposure levels associated with pre-harvest agricultural burning of sugarcane and with sugar processing in the factory pose a potential hazard to human health, particularly chronic exposures in occupational scenarios. The concentrations of PM₁₀ measured in this study were typically less than current occupational PEL limits (OSHA) and ambient PM₁₀ guidelines issued by the WHO, however, more research is needed to constrain the health impacts from long term exposure to relatively low levels of PM. Although the airborne PM and ash deposits are mostly carbonaceous matter and silicate minerals (in addition to the uncharacterized organic compounds), airborne PM samples captured during burning and harvesting were found to be within the ultra-fine and fine range, which can be inhaled deep into the alveolar region of the lung. Mineral particles present in a respirable size in airborne PM samples could also contribute to respiratory ill health, and the presence of fibrous PM must be further investigated.

Ash that has been distributed into the fields and waste piles may be easily broken down into respirable-size PM, promoting its re-suspension into the atmosphere, for example, during cutting of the sugarcane in the fields after burning events. The ash from sugarcane trash therefore also represents a potential source of respirable airborne particulate, which local populations and

workers may be exposed to over extended periods of time. Sugarcane processing and the associated activities create PM that should be considered both an acute and chronic respiratory hazard. The physicochemical properties (such as chemical composition and surface reactivity) of the ash deposits must be taken into account when a health assessment is made, especially given that a predicted increase in sugarcane production for biofuel is likely to be associated with increasing quantities of ash residue.

Acknowledgements

JSL's work was supported by a JRF at Imperial College London and a NERC studentship (NER/S/A/2006/14107). CJH acknowledges a NERC Postdoctoral Research Fellowship (NE/C518081/2). We thank A. Cardoso, at UNESP, Brazil for fieldwork assistance and the Farm Managers, who allowed us to collect data and samples in Brazil and Ecuador.

References

- ACSM (American College of Sports Medicine), 2006. *Metabolic Calculations Handbook*. Lippincott Williams and Wilkins, US.
- ACGIH, 2006. *Threshold Limit Values (TLVs) and Biological Exposure Indices (BEIs)*. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.
- Allen, A.G., Cardoso, A.A., da Rocha, G.O., 2004. Influence of sugar cane burning on aerosol soluble ion composition in Southeastern Brazil. *Atmos. Environ.* 38, 5025–5038.
- Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. *Glob. Biogeochem. Cy.* 15 (4), 955–966.
- Arbex, M.A., Saldiva, P.H.N., Pereira, L.A.A., Braga, A.L.F., 2010. Impact of outdoor biomass air pollution on hypertension hospital admissions. *J. Epidemiol. Community Health* 64 (7), 573–579.
- Arbex, M.A., Martins, L.C., Oliveira, R.C., Pereira, L.A.A., Arbex, F.F., Cançado, J.E.D., Saldiva, P.H.N., Braga, A.L.F., 2007. Air pollution from biomass burning and asthma hospital admissions in a sugar cane plantation area in Brazil. *J. Epidemiol. Commun. H.* 61, 395–400.
- Arbex, M.A., Böhm, G.M., Saldiva, P.H.N., Conceição, G.M.S., Pope III, C.A., Braga, A.L.F., 2000. Assessment of the effects of sugar cane plantation burning on daily counts of inhalation therapy. *J. Air Waste Manag.* 50, 1745–1749.
- Barbosa, C.M., Terra-Filho, M., de Albuquerque, A.L., Di Giorgi, D., Grupi, C., Negrao, C.E., Rondon, M.U., Martinez, D.G., Marcourakis, T., dos Santos, F.A., Braga, A.L., Zanetta, D.M., Santos, U.deP., 2012. Burnt sugarcane harvesting - cardiovascular effects on a group of healthy workers, Brazil. *PLoS One* 7 (9), e46142. <http://dx.doi.org/10.1371/journal.pone.0046142>.
- Bilba, K., Ouensanga, A., 1996. A Fourier transform infrared spectroscopy study of thermal degradation of sugar cane bagasse. *J. Anal. Appl. Pyrol.* 38, 61–73.
- Brochu, P., Ducré-Robitaille, J.-F., Brodeur, J., 2006. Physiological daily inhalation rates for free-living individuals aged 2.6 months to 96 years based on doubly labeled water measurements: comparison with time-activity-ventilation and metabolic energy conversion estimates. *Hum. Ecol. Risk Assess.: Int. J.* 12 (4), 736–761.
- Brown, J.S., Gordon, T., Price, O., Asgharian, B., 2013. Thoracic and respirable particle definitions for human health risk. *Part. Fibre Toxicol.* 10, 12. <http://dx.doi.org/10.1186/1743-8977-10-12>.
- Carvalho, J.L.N., Otto, R., Coutinho, H., Franco, J., Trivelin, P.C.O., 2013. Input of sugarcane post-harvest residues into the soil. *Sci. Agric.* 70 (5), 336–344.
- Carvalho-Oliveira, R., Pozo, R.M.K., Lobo, D.J.A., Lichtenfels, A.J.F.C., Martins-Junior, H.A., Bustilho, J.O.V., Saiki, M., Sato, I.M., Saldiva, P.H.N., 2005. Diesel emissions significantly influence composition and mutagenicity of ambient particles: a case study in São Paulo, Brazil. *Environ. Res.* 98, 1–7.
- Cançado, J.E.D., Saldiva, P.H.N., Pereira, L.A.A., Lara, L.B.L.S., Artaxo, P., Martinelli, L.A., Arbex, M.A., Zanobetti, A., Braga, A.L.F., 2006. The impact of sugar cane burning emissions on the respiratory system of children and the elderly. *Environ. Health Persp.* 114 (5), 725–729.
- Caetano-Silva, L., Allen, A.G., Lima-Souza, M., Cardoso, A.A., Campos, M.L.A.M., Nogueira, R.F.P., 2013. An analysis of diurnal cycles in the mass of ambient aerosols derived from biomass burning and agro-industry. *J. Geophys. Res. Atmos.* 118 (15), 8675–8687.
- Cashier, H., 1998. Carbonaceous combustion particles. In: Harrison, R.M., Van Grieken, R.E. (Eds.), *Atmospheric Particles*. Wiley-Interscience, New York, pp. 295–348.
- Chargas, M.F., Bordonal, R.O., Cavalett, O., Carvalho, J.L.N., Bonomi, A., La Scala Jr., N., 2016. Environmental and economic impacts of different sugarcane productions systems in the ethanol biorefinery. *Biofuels Bioprod. Biorefining* 10 (1), 89–106.
- Cherrie, J.W., Brosseau, L.M., Hay, A., Donaldson, K., 2013. Low-toxicity dusts: current exposure guidelines are not sufficiently protective. *Ann. Occup. Hyg.* 57 (6), 685–691.
- Committee of the Environmental and Occupational Health Assembly of the American Thoracic Society, 1996. Health effects of outdoor air pollution. *Am. J. Respir.*

- Crit. Care Med. 153 (1), 3–50.
- Companhia Ambiental do Estado de São Paulo (CETESB), 1997. Relatório de qualidade do ar no Estado de São Paulo, 1996. CETESB, São Paulo, Brazil.
- Conceição, G.M.S., Miraglia, S.G.E.K., Kishi, H.S., Saldiva, P.H.N., Siner, J.M., 2001. Air pollution and child mortality: a time-series study in São Paulo. *Braz. Environ. Health Persp.* 109 (3), 347–350.
- Crowe, J., van Wendel de Joode, B., Wesseling, C., 2009. A Pilot Field Evaluation on Heat Stress in Sugarcane Workers in Costa Rica: what to Do Next? *Global Health Action*, 2. <http://www.globalhealthaction.net/index.php/gha/article/view/2062/2560>.
- Cyr, M., Tagnit-Hamou, A., 2001. Particle size distribution of fine powders by LASER diffraction spectroscopy. Case of cementitious materials. *Mater. Struct.* 34, 342–350.
- Das, P., Ganesh, A., Wangikar, P., 2004. Influence of pretreatment for de-ashing of sugarcane bagasse on pyrolysis products. *Biomass Bioenerg.* 27 (5), 445–457.
- Dawson, L., Boopathy, R., 2007. Use of post-harvest sugarcane residue for ethanol production. *Bioresour. Technol.* 98, 1695–1699.
- Derbyshire, E., Horwell, C., Jones, T.J., Tetley, T.J., 2012. Airborne particles. In: Plant, J., Voulvoulis, N., Ragnarsdottir, K.V. (Eds.), *Pollutants, Human Health and the Environment: a Risk Based Approach*. John Wiley and Sons Ltd, pp. 255–286.
- Figueiredo, E.B., La Scala Jr., N., 2011. Greenhouse gas balance due to the conversion of sugarcane areas from burned to green harvest in Brazil. *Agriculture. Ecosyst. Environ.* 141 (1–2), 77–85.
- Fonseca, A.S., Talbot, N., Schwarz, J., Ondráček, J., Ždímal, V., Kozáková, J., Viana, M., Karanasiou, A., Querol, X., Alastuey, A., Vu, T.V., Delgado-Saborit, J.M., Harrison, R.M., 2016. Intercomparison of four different cascade impactors for fine and ultrafine particle sampling in two European locations. *Atmos. Chem. Phys. Discuss.* <http://dx.doi.org/10.5194/acp-2015-1016>.
- França, D., Longo, K., Rudorff, B., Aguiar, D., Freitas, S., Stockler, R., Pereira, G., 2014. Pre-harvest sugarcane burning emission inventories based on remote sensing data in the state of São Paulo, Brazil. *Atmos. Environ.* 99, 446–456.
- Frías, M., Villar-Cociña, E., Valencia-Morales, E., 2007. Characterisation of sugar cane waste as pozzolanic material for construction: calcining temperature and kinetic parameters. *Waste Manag.* 27, 533–538.
- García-Pérez, M., Chaala, A., Pakdel, H., Roy, C., 2002. Sugarcane bagasse vacuum pyrolysis. *J. Anal. Appl. Pyrol.* 65, 111–136.
- Gasparatos, A., Borzoni, M., Abramovay, R., 2012. The Brazilian bioethanol and biodiesel programs: drivers, policies, and impacts. In: Gasparatos, A., Stromberg, P. (Eds.), *Socioeconomic and Environmental Impacts of Biofuels: Evidence from Developing Nations*. Cambridge University Press, pp. 111–143.
- Gwaze, P., Schmid, O., Annegarn, H.J., Andrae, M.O., Huth, J., Helas, G., 2006. Comparison of three methods of fractal analysis applied to soot aggregates from wood combustion. *J. Aerosol Sci.* 37, 820–838.
- Hayes, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullet, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. *Atmos. Environ.* 39, 6747–6764.
- Hearn, C.E.D., 1968. Bagassosis, an epidemiological environmental and clinical survey. *Brit. J. Ind. Med.* 25, 283–292.
- International Energy Agency (IEA), 2004. *Biofuels for Transport: an International Perspective*. OECD/IEA, Paris.
- Jacobson, L.D.S.V., Hacon, S.D.S., Castro, H.A.d., Ignotti, E., Artaxo, P., Saldiva, P.H.N., Leon, A.C.M.Pd., 2014. Acute effects of particulate matter and black carbon from seasonal fires on peak expiratory flow of schoolchildren in the Brazilian Amazon. *PLoS One* 9 (8), e104177. <http://dx.doi.org/10.1371/journal.pone.0104177>.
- Jimenez, J., Wu, C.-F., Claiborn, C., Gould, T., Simpson, C.D., Larson, T., Sally Lui, L.J., 2006. Agricultural burning smoke in Eastern Washington – part 1: atmosphere characterisations. *Atmos. Environ.* 40, 639–650.
- Kingham, S., Durand, M., Aberkane, T., Harrison, J., Gains Wilson, J., Epton, M., 2006. Winter comparison of TEOM, MiniVol and DustTrak PM₁₀ monitors in a woodsmoke environment. *Atmos. Environ.* 40, 338–347.
- Kingston, G., Donzelli, J.L., Meyer, J.H., Richards, E.P., Seeruttun, S., Torres, J., Van Antwerpen, R., 2005. Impact of the green-cane harvesting on planting and crop re-establishment: an overview. *Proc. ISSCT* 15, 521–533.
- Kuempel, E.D., O'Flaherty, E.J., Stayner, L.T., Smith, R.J., Green, F.H., Vallyathan, V., 2001. A biomathematical model of particle clearance and retention in the lungs of coal miners. *Regul. Toxicol. Pharmacol.* 34 (1), 69–87.
- Lambert, M.I., Cheevers, E.J., Coopoo, Y., 1994. Relationship between energy expenditure and productivity of sugar cane cutters and stackers. *Occup. Med.-C* 44, 190–194.
- Lara, L.L., Artaxo, P., Martinelli, L.A., Camargo, P.B., Victoria, R.L., Ferraz, E.S.B., 2005. Properties of aerosols from sugar cane burning emissions in Southeastern Brazil. *Atmos. Environ.* 39, 4627–4637.
- Le Blond, J.S., Horwell, C.J., Williamson, B.J., Oppenheimer, C., 2010. Generation of crystalline silica from sugarcane burning. *J. Environ. Monit.* 12, 1459–1470.
- Le Blond, J.S., Williamson, B.J., Horwell, C.J., Monro, A.K., Kirk, C.A., Oppenheimer, C., 2008. Production of potentially hazardous respirable silica airborne particulate from the burning of sugarcane. *Atmos. Environ.* 42 (22), 5558–5568.
- Li, J., Pósfai, M., Hobbs, P.V., Buseck, P.R., 2003. Individual aerosol particles from biomass burning in southern Africa: 2. Composition and ageing of inorganic particles. *J. Geophys. Res.* 108 (D13), 8484. <http://dx.doi.org/10.1029/2002JD002310>.
- Liu, L.J.S., Slaughter, J.C., Larson, T.V., 2002. Comparison of light scattering devices and impactors for particulate measurements in indoor, outdoor, and personal environments. *Environ. Sci. Technol.* 36, 2977–2986.
- Liu, X., Van Espen, P., Adams, F., Cafmeyer, J., Maenhaut, W., 2000. Biomass burning in Southern Africa: individual particle characterisation of atmospheric aerosols and savannah fire samples. *J. Atmos. Chem.* 36 (2), 135–155.
- Long, W.L., Tate, R.B., Neuman, M., Mafred, J., Becker, A.B., Athonisen, N.R., 1998. Respiratory symptoms in a susceptible population due to burning of agricultural residue. *Chest* 113 (2), 351–357.
- Lopes, F.S., Ribeiro, H., 2006. Mapeamento de internações hospitalares por problemas respiratórios e possíveis associações à exposição humana aos produtos da queima da palha de cana-de-açúcar no estado de São Paulo. *Rev. Bras. Epidemiol.* 9 (2), 215–225.
- Macedo, I.C., Seabra, J.E.A., Silva, J.E.A.R., 2008. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: the 2005/2006 averages and prediction for 2020. *Biomass Bioenergy* 32, 582–595.
- Machlis, G.E., 2002. Burning Questions: a Social Science Research Plan for Federal Wildland Fire Management. Report to the National Wildfire Coordinating Group. University of Idaho, Moscow, p. 253.
- Mazzoli-Rocha, F., Oliveira, V.R., Barcellos, B.C., Moreira, D.K.M., Saldiva, P.H.N., Faffe, D.S., Zin, W.A., 2016. Time-dependency of mice lung recovery after a 4-week exposure to traffic or biomass air pollutants. *Respir. Physiol. Neurobiol.* 230, 16–21.
- Mazzoli-Rocha, F., Carvalho, G.M.C., Lanzetti, M., Valença, S.S., Silva, L.F.F., Saldiva, P.H.N., Zin, W.A., Faffe, D.S., 2014. Respiratory toxicity of repeated exposure to particles produced by traffic and sugar cane burning. *Respir. Physiol. Neurobiol.* 191, 106–113.
- Mbendge, S., Alleman, L.Y., Flament, P., 2015. Bioaccessibility of trace elements in fine and ultrafine atmospheric particles in an industrial environment. *Environ. Geochem. Health* 37 (5), 875–889.
- Mnatzaganian, C.L., Pellegrin, K.L., Miyamura, J., Valencia, D., Pang, L., 2015. Association between sugar cane burning and acute respiratory illness on the island of Maui. *Environ. Health* 14, 81. <http://dx.doi.org/10.1186/s12940-015-0067-y>.
- Morawska, L., Thomas, S., Bofinger, N.D., Wainwright, D., Neale, D., 1998. Comprehensive characterization of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants. *Atm. Environ.* 32, 2461–2478.
- Morfeld, P., Bruch, J., Levy, L., Ngiewih, Y., Chaudhuri, I., Muranko, H.J., Myerson, R., McCunney, R.J., 2015. Translational toxicology in setting occupational exposure limits for dusts and hazard classification – a critical evaluation of a recent approach to translate dust overload findings from rats. *Part. Fibre Toxicol.* 12, 3. <http://dx.doi.org/10.1186/s12989-015-0079-3>.
- Morfeld, P., 2013. Exposure-response association between cumulative exposure to respirable crystalline silica dust and lung cancer. *Zbl Arbeitsmed Arbeitsschutz Ergon.* 63 (4), 342–346.
- Morgan, W., Seaton, A., 1984. In: Saunders, W.B. (Ed.), *Occupational Lung Diseases*, second ed. Philadelphia, US.
- Morrison, J.F., Blake, G.T.W., 1974. Physiological observations on cane cutters. *Eur. J. Appl. Physiol.* 33, 247–254.
- Müller, M.L., Coetsee, M.F., 2008. Physiological demands and working efficiency of sugarcane cutters in harvesting burnt and unburnt cane. *Int. J. Ind. Ergon.* 38 (3–4), 314–320.
- Muñoz, O., Volten, H., de Haan, J.F., Vassen, W., Hovenier, J.W., 2001. Experimental determination of scattering matrices of randomly oriented fly ash and clay particles at 442 and 633 nm. *J. Geophys. Res.* 106 (D19), 22833–22844. <http://dx.doi.org/10.1029/2000JD00164>.
- Nicoletta, A.C., Belluzzo, W., 2015. The effect of reducing the pre-harvest burning of sugarcane on respiratory health in Brazil. *Environ. Dev. Econ.* 20 (10), 127–140.
- Nunes Jr., D., Gonçalves, J.L., da Silva Jr., A.C., 2014. Nagumo Mand d'Aragão RB, Indicadores de Desempenho da Agroindústria Canavieira – Safras 2012/13 e 2013/14. IDEA – Instituto de Desenvolvimento Agroindustrial, Ribeirão Preto, SP, p. 155.
- Obernberger, I., Brunner, T., 2005. *Aerosols in Biomass Combustion*. University of Graz, Institute for Resource Efficient and Sustainable Systems, Graz, Austria.
- Occupational Safety and Health Administration (OSHA), 2006. 1910.1000, Table Z-1 Limits for Air Contaminants. https://www.osha.gov/pls/oshweb/owadisp.show_document?p_table=STANDARDS&p_ID=9992 (Last accessed 19 July 2016).
- Oliveira, M.W., Trivelin, P.C.O., Penatti, C.P., Piccollo, M.C., 1999. Straw mineralization and root growth of sugarcane as related to nitrogen fertilization at planting. *Pesqui. Agropecuária Bras.* 34, 2359–2362.
- Osto, B., 2004. Outdoor Air Pollution: Assessing the Environmental Burden of Disease at National and Local Levels. World Health Organisation, Geneva, 2004 (WHO Environmental Burden of Disease Series, No. 5).
- Phoolchund, H.N., 1991. Aspects of occupational health in the sugar cane industry. *J. Soc. Occup. Med.* 41 (3), 133–136.
- Pósfai, M., Simonic, R., Li, J., Hobbs, P.V., Buseck, P.R., 2003. Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles. *J. Geophys. Res.* 108 (D13), 8483. <http://dx.doi.org/10.1029/2002JD002291>.
- Prove, B.G., Doogan, V.J., Truong, P.N.V., 1995. Nature and magnitude of soil erosion in sugarcane land on the wet tropical coast of north-eastern Queensland. *Aust. Exp. Agric.* 35, 641–649.
- Quality of Urban Air Review Group (QUARG), 1996. *Airborne Particulate Matter in the United Kingdom, Third Report of the Quality of Urban Air Review Group*. Department of the Environment, Belfast, p. 30.
- Ribeiro, H., 2008. Sugar cane burning in Brazil: respiratory health effects. *Rev. Saúde*

- Pública 42 (2), 1–6.
- Robertson, F.A., Thornburn, P.J., 2007. Decomposition of sugarcane harvest residue in different climatic zones. *Aust. J. Soil Res.* 45, 1–11.
- Rudorff, B.F.T., Aguiar, D.A., Silva, W.F., Sugawara, L.M., Adami, M., Moreira, M.A., 2010. Studies on the rapid expansion of sugarcane for ethanol productions in São Paulo State (Brazil) using Landsat data. *Remote Sens. Environ.* 112, 271102726.
- Saldiva, P.H.N., Lichtenfels, A.J.F.C., Paiva, P.S.O., Barone, I.A., Martins, M.A., Massad, E., Pereira, J.C.R., Xavier, V.P., Singer, J.M., Bohm, G.M., 1994. Association between air pollution and mortality due to respiratory diseases in children in São Paulo. *Braz. J. Prelim. Rep. Environ. Res.* 65, 218–225.
- Scovronick, N., França, D., Alonso, M., Almeida, C., Longo, K., Freitas, S., Rudorff, B., Wilkinson, P., 2016. Air quality and health impacts of future ethanol production and use in São Paulo state. *Braz. Int. J. Environ. Res. Public Health* 13 (7), 695. <http://dx.doi.org/10.3390/ijerph13070695>.
- Silva, T.H.G., Carvalho, A.P.F., Milani, T.M.S., Mauad, T., Saldiva, P.H.N., Borges, M.C., 2015. Composition of sugar cane burning particles and its effects in an animal model of allergic asthma. *Am. J. Respir. Crit. Care Med.* 191. Meeting abstract: A1724.
- Silveira, H.C.S., Schmidt-Carrio, M., Seidel, E.H., Scapulatempo-Neto, C., Longatto-Filho, A., Carvalho, A.L., Reis, R.M.V., Saldiva, P.H.N., 2013. Emissions Generated by Sugarcane Burning Promote Genotoxicity in Rural Workers: a Case Study in Barretos, Brazil, vol. 12, p. 87. <http://dx.doi.org/10.1186/1476-069X-12-87>.
- Sioutas, C., 2004. Development of New Generation Personal Monitors for Fine Particulate Matter (PM) and its Metal Content. NUATRC Research Report No. 2.
- SKC, 2004. IP-10A Method Update. Determination of Fine Particulate Matter in Indoor Air Using Size-specific Impaction. Publication No. 1660, issue 0601. <http://www.skcinco.com/instructions/IP10A.pdf> (Last accessed Jan 2010).
- Souza, L.S., Nascimento, L.F., 2016. Air pollutants and hospital admission due to pneumonia in children: a time series analysis. *Rev. Assoc. Med. Bras.* 62 (2), 151–156.
- Souza, D.Z., Vasconcellos, P.C., Lee, H., Aurela, M., Saarnio, K., Teinilä, K., Hillamo, R., 2014. Composition of PM_{2.5} and PM₁₀ collected at urban sites in Brazil. *Aerosol Air Qual. Res.* 14, 168–176.
- Spurr, G.B., Barac-Nieto, M., Maksud, M.G., 1977. Productivity and maximal oxygen consumption in sugar cane cutters. *Am. J. Clin. Nutr.* 30, 316–321.
- Stayner, L.T., Graber, J.M., 2011. Does exposure to coal dust prevent or cause lung cancer? *Occup. Environ. Med.* 68 (3), 167–168.
- Schwartz, J., Slater, D., Larson, T.V., Pierson, W.E., Koenig, J.Q., 1993. Particulate air pollution and hospital emergency room visits for asthma in Seattle. *Am. Rev. Respir. Dis.* 147 (7), 826–831.
- Thornburn, P.J., Probert, M.E., Robertson, F.A., 2001. Modeling decomposition of sugar cane surface residues with APSIM-Residue. *Field Crops Res.* 70 (3), 223–232.
- Tran, C.L., Buchanan, D., 2000. Development of a Biomathematical Lung Model to Describe the Exposure-dose Relationship for Inhaled Dust Among U.K. Coal Miners. Research Report TM/00/02 April 2000. Institute of Occupational Medicine, Edinburgh, U.K.
- Umbuzeiro, G.A., Franco, A., Magalhães, D., Castro, F.J.V., Kummrow, F., Rech, C.M., Carvalho, L.F., Vasconcellos, P.C., 2008. A preliminary characterization of the mutagenicity of atmospheric particulate matter collected during sugar cane harvesting using the Salmonella/microsome microsuspension assay. *Environ. Mol. Mutagen.* 49, 249–255.
- Uriarte, M., Yackulic, C.B., Flynn, D., Cortes, M., Crk, T., Cullman, G., McGinty, M., Sircely, J., 2009. Expansion of sugarcane production in São Paulo, Brazil: implications for fire occurrence and respiratory health. *Agric. Ecosyst. Environ.* 132, 48–56.
- U.S. Environmental Protection Agency (US EPA), 2013. National ambient air quality standards for particulate matter; final rule. *Fed. Regist.* 78 (Jan 15), 3086–3287.
- U.S. Environmental Protection Agency (US EPA), 1998. Particulate Matter Research Needs for Human Health Risk Assessment to Support Future Reviews of the National Ambient Air Quality Standards for Particulate Matter. National Center for Environmental Assessment. Research Triangle Park, NC 27711, EPA/600/R-97/137F.
- U.S. Environmental Protection Agency (US EPA), 1987. Revisions to the national ambient air quality standards for particulate matter. *Fed. Regist.* 52 (July 1), 24634–24669.
- Vasconcellos, P.C., Souza, D.Z., Sanchez-Ccoyllo, O., Bustillos, J.O.V., Lee, H., Santos, F.C., Nascimento, K.H., Araújo, M.P., Saarnio, K., Teinila, K., Hillamo, R., 2010. Determination of anthropogenic and biogenic compounds on atmospheric aerosol collected in urban, biomass burning and forest areas in São Paulo. *Braz. Sci. Total Environ.* 408, 5836–5844.
- Ward, D.E., 1990. Factors influencing the emissions of gases and particulate matter from biomass burning. In: Goldammer, J.G. (Ed.), *Fire in the Tropical Biota*. Springer-Verlag, pp. 418–436.
- Wentzel, M., Gorzawski, H., Naumann, K.-H., Saathoff, H., Weinbruch, S., 2003. Transmission electron microscopical and aerosol dynamic characterisation of soot aerosols. *J. Aerosol Sci.* 34, 1347–1370.
- World Health Organization (WHO), 2005. WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. Global Update. Summary of Risk Assessment (WHO/SDE/PHE/OEH/06.02). World Health Organization, Geneva.
- WHO, 1986. Asbestos and Other Natural Mineral Fibres. Environmental Health Criteria 53. WHO, Geneva.
- Zanderons, J., Gravitis, J., Kokorevics, A., Zhurinsk, A., Bikovens, O., Tardenaka, A., Spince, B., 1999. Studies of the Brazilian sugarcane bagasse carbonisation process and products properties. *Biomass Bioenerg.* 17, 209–219.